TiO_2-AC hybrid materials to produce H_2 and biogas by photocatalytic decomposition of acetic acid.

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Hybrid TiO_2-AC photocatalysts were prepared by the addition of different percentages (0, 0.5, 1 and 10 wt. %) of a self-prepared activated carbon (AC) to a sol-gel synthesis mixture based on titanium tetraisopropoxide. This AC was prepared by hydrothermal synthesis of saccharose and its morphology is spherical. The characterization (gas adsorption, XRD) has shown that the TiO_2-AC samples are mainly amorphous, with surface areas above 300 m^2/g. These photocatalysts were tested in the decomposition of acetic acid in aqueous solution, showing that all the prepared materials are more active than commercial TiO_2 P25, and the presence of AC improves the activity of pure TiO_2. The catalyst with 0.5 wt. % AC is the most active. The presence of carbon likely decreases the electron/hole pairs' recombination and favors the substrate adsorption. However, a large amount of carbon has also the negative effect of a strong light adsorption.

1. Scope

TiO_2 is one of the most investigated photocatalysts, although its efficiency should still be improved. Among the different available strategies to address this issue, the combination of TiO_2 with carbon seems to lead to an increased activity. Such a combination can be achieved by different methods that result in quite different TiO_2-C systems[1]. The present work focuses on the preparation of TiO_2-AC samples by a method based on the synthesis of TiO_2 by sol-gel in the presence of a spherical activated carbon that had been previously obtained by hydrothermal treatment of saccharose. The photocatalysts are tested in the challenging process of acetic decomposition, with the purpose of obtaining biogas and hydrogen from polluted wastewater.

2. Results and discussion

TiO_2-AC materials were prepared using an activated carbon previously synthesised by hydrothermal treatment of saccharose (1.6 M aqueous saccharose solution, 180 ºC, 12 h, followed by washing and drying at 110 ºC, 5 h) and activation with CO_2 (80 ml/min, 5 ºC/min up to 800 ºC, 10 h)[2]. This AC presents spherical morphology (Figure 1), and the sol-gel conditions used to prepare the TiO_2-AC catalysts are summarized in the following: 9.3 ml titanium tetraisoproxide were mixed with 17.5 ml acetic acid and 197.5 ml H_2O drop by drop. During the H_2O addition, different amounts of the spherical AC were added to the reaction mixture (to achieve 0, 0.5, 1 and 10 wt. %). These photocatalysts were characterized by gas adsorption (N_2 and CO_2 at -196 ºC and 0 ºC, respectively, Autosorb-6B (Quantachrome) and XRD (Miniflex II Rigaku).

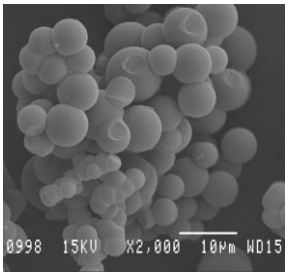

Figure 1. SEM images of the synthesized AC.

The photodecomposition of acetic acid was performed in the following conditions: 350 mg catalyst, 250 ml of 1M aqueous acetic acid solution and illumination with 365 nm wavelength mercury lamp for 12 h. The reaction products, mainly CH_4, CO_2 and H_2, were quantified by mass spectrometry.

Table 1 shows the textural properties of the obtained materials together with those of commercial TiO_2 P25 (Evonik). It can be observed that the prepared AC has a large surface area, about 1500 m^2/g. Pure TiO_2 and the TiO_2-AC materials show similar surface areas, in the range of 300 m^2/g, larger than P25. Both pure TiO_2 and the TiO_2-AC materials are essentially amorphous, with a low amount of crystalline anatase (around 6 %). XRD

data (Table 1) show that mean anatase crystal size in the synthesized samples is much smaller than in the reference material P25.

Figure 2 compiles the obtained photocatalytic activity data (as amount of CH_4, CO_2 and H_2 produced) and the results of a blank experiment which shows the photolysis[3] of acetic acid in these conditions. It can be observed that the photocatalysts prepared in this work, both without or with AC, show higher activity than the P25 reference catalyst. The three TiO_2-AC catalysts are more active than pure TiO_2, but the amount of AC present in the samples significantly affects the catalytic activity, being sample TiO_2-AC-10 only slightly more active than TiO_2, while sample TiO_2-AC-0.5 is noticeably more active (1.6 times more active). In general, the effect of the AC is associated to either an increase in the adsorption capacity of the materials or to a decrease in the recombination rate of the electron/hole photogenerated pairs[5]. These results show that a small amount of AC (around 0.5 wt. %) leads to these positive effects, which seem to be diminished when the amount of carbon is higher; a phenomenon that can be related with the strong light absorption of carbon materials[5].

Table 1. Textural properties and mean anatase crystal size in the prepared samples.

Sample	S_{BET} (m^2/g)	V_{N2} (cm^3/g)	V_{CO2} (cm^3/g)	Anatase crystal size (nm)
AC	491	0.25	0.27	--
P25	60	0.02	0.02	22
TiO_2	309	0.11	0.09	7
TiO_2-AC-0.5	290	0.11	0.04	5
TiO_2-AC-1	332	0.12	0.04	6
TiO_2-AC-10	292	0.11	0.06	6

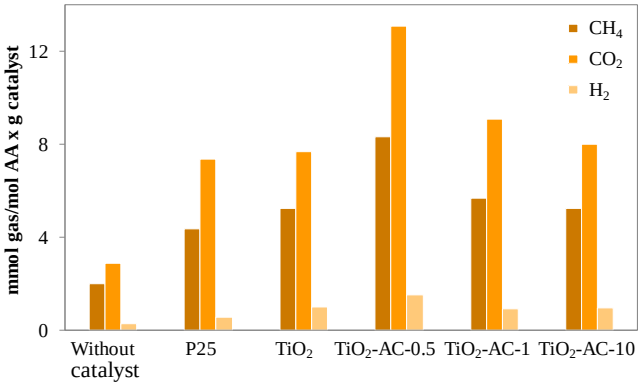

Figure 2. CH_4, CO_2 and H_2 produced in a blank experiment without catalyst, with TiO_2 P25 and with the prepared catalysts.

3. Conclusions

TiO_2-AC hybrid materials have been synthesized by incorporating different amounts of a spherical activated carbon obtained from saccharose by hydrothermal treatment during the synthesis of TiO_2 by the sol-gel method. Despite their low crystallinity, these materials have shown to be active in the photocatalytic decomposition of acetic acid, producing biogas and hydrogen, and this can be related to their high specific surface area. The results show that the presence of the spherical activated carbon markedly favors the catalytic efficiency, being the sample with the lower carbon content (0.5 wt.%) the one leading to the best results. This small amount of carbon seems to decreases the electron/hole pairs' recombination and to favor the substrate adsorption without the negative effect of a strong light adsorption.

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References

1. L. Gomathi Devi, R. Kavitha, *Appl. Catal. B Environ.*, **2013**, 140-141, 559-587.
2. A.J. Romero-Anaya, M. Ouzzine, M.A. Lillo-Ródenas, A. Linares-Solano, *Carbon*, **2014**, 68, 296-307.
3. G.L. Hung, J. Bartoszewicz, H. Kozubed, M. Pietrzak, J. Paczkowski, B. Marciniak, *J. Photochem. Photobiol. A Chem.* **2008**, 198, 250-255.
4. R. Marschall, L. Wang, *Catal. Today*. **2014**, 225, 111-135.
5. R. Kavitha, L.G. Devi, *J. Environ. Chem. Eng*. **2014**, 2, 857-867.